Supporting Information

For

Evolution of Single Chain Conformation for Model Comb-like Chains with Grafting Density Ranging from 0 to ~100% in Dilute Solution

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¹Department of Chemical Physics, University of Science and Technology of China, Hefei, China 230026 ²Food Science and Processing Research Center, Shenzhen University, Shenzhen, China 518060 ³Institute for Advanced Study, Shenzhen University, Shenzhen, China 518060 Calculation of dn/dc Values for Comb-like Chains with Different Grafting Density. In this work, we used the classical additive rule to extract $(dn/dc)_{comb}$ for PPA_{Nb}-g-PS₃₀- σ , i.e., $(dn/dc)_{comb} = wt\%_{graft}(dn/dc)_{graft} + wt\%_{backbone}(dn/dc)_{backbone}$, where $wt\%_{graft}$ and $wt\%_{backbone}$ represents the mass fractions for graft and backbone, respectively. Herein, $(dn/dc)_{graft}$ and $(dn/dc)_{backbone}$ are known parameters. Although $wt\%_{graft} + wt\%_{backbone} = 1.0$, neither $wt\%_{graft}$ nor $wt\%_{backbone}$ is pre-unknown. How to find a solution to such a "deadknot"?

For a sample with known N_g and N_b , it is not difficult to realize that all composition-related parameters are intrinsically correlated. In other words, for parameters $wt\%_{graft}$, $wt\%_{backbone}$, M_{comb} , $(dn/dc)_{comb}$ and σ , as long as one of them is given, the others should be easily deduced out from a perspective of mathematics. Specifically, by treating σ as independent variable, the others can be expressed as $wt\%_{graft} = \psi(\sigma)$, $wt\%_{backbone} = 1 - \psi(\sigma)$, $M_{comb} = f(\sigma)$ and $(dn/dc)_{comb}$ $= \chi(\sigma)$. Specifically, these correlation equations could be expressed as

$$wt\%_{\text{graft}} = 1 - wt\%_{\text{backbone}} = 1 - \frac{N_{\text{b}}M_{0,\text{b}}}{N_{\text{b}}M_{0,\text{b}} + N_{\text{b}}\sigma N_{\text{g}}M_{0,\text{g}}} = \frac{N_{\text{b}}\sigma N_{\text{g}}M_{0,\text{g}}}{N_{\text{b}}M_{0,\text{b}} + N_{\text{b}}\sigma N_{\text{g}}M_{0,\text{g}}}$$
(S1)

$$M_{\rm comb} = N_{\rm b}M_{0,\rm b} + N_{\rm b}\sigma N_{\rm g}M_{0,\rm g} \tag{S2}$$

$$(dn / dc)_{\text{comb}} = wt \%_{\text{backbone}} (dn / dc)_{\text{backbone}} + wt \%_{\text{graft}} (dn / dc)_{\text{graft}} \frac{N_{\text{b}} M_{0,\text{b}}}{N_{\text{b}} M_{0,\text{b}} + N_{\text{b}} \sigma N_{\text{g}} M_{0,\text{g}}} (dn / dc)_{\text{backbone}} + \frac{N_{\text{b}} \sigma N_{\text{g}} M_{0,\text{g}}}{N_{\text{b}} M_{0,\text{b}} + N_{\text{b}} \sigma N_{\text{g}} M_{0,\text{g}}} (dn / dc)_{\text{graft}}$$
(S3)

Following a similar rule, by combining eqs 1-3, M_{comb} can be also represented by a function of $(dn/dc)_{\text{comb}}$ as

$$M_{\rm comb} = N_{\rm b} M_{0,\rm b} \frac{\left(\frac{dn}{dc}\right)_{\rm graft} - \left(\frac{dn}{dc}\right)_{\rm backbone}}{\left(\frac{dn}{dc}\right)_{\rm graft} - \left(\frac{dn}{dc}\right)_{\rm comb}}$$
(S4)

 $M_{0,b}$: the molar mass of a monomer unit on backbone, and $M_{0,b} = 243$ g/mol. $M_{0,g}$: the molar mass of a monomer unit on sidechain and $M_{0,g} = 104$ g/mol. M_{comb} : the average molar mass of the comb-like polymers. wt_{backbone} : the mass percentage of backbone. *wt*%_{graft}: the mass percentage of sidechain.

 $(dn/dc)_{comb}$: the refractive index increment of comb-like polymers.

 $(dn/dc)_{backbone}$: the refraction index increment of backbone, and $(dn/dc)_{backbone} = 0.157 \text{ mL/g}$.

 $(dn/dc)_{graff}$: the refraction index increment of sidechain, and $(dn/dc)_{graff} = 0.187 \text{ mL/g}$.

 N_b : the number average degree of polymerization of backbone, where $N_b = 80$, 585, 1010 and 2500 were used in the calculation. Note that the number average values have to be used according to the physical meaning of classical additive rule.

 $N_{\rm g}$: the number average degree of polymerization of sidechain, where $N_{\rm g} = 26$ were used in the calculation.

Obviously, all involved parameters are known except $(dn/dc)_{comb}$. On the other hand, we do know that the output value of M_w is inversely proportional to the input value of $(dn/dc)_{comb}$ during the analysis process of TD-SEC data, which further leads to

$$M_{\rm comb} = \Gamma / [(dn/dc)_{\rm comb}]$$
(S5)

where the pre-factor Γ is a feature parameter and Γ possesses a unique numerical value for a specific sample. More importantly, Γ for each PPA_{Nb}-g-PS₃₀- σ sample can be easily determined in TD-SEC measurement. By comparing eqs S4 and S5, the point of intersection of two function curves leads to the true values of $(dn/dc)_{comb}$ and M_{comb} for a specific sample. Figure S8 shows one typical example of how to calculate $(dn/dc)_{comb}$ values for PPA₁₀₅₅-g-PS₃₀- σ samples.

Experimental Section

Materials. Unless stated otherwise, all chemicals were obtained from commercial suppliers and were used as received. Tert-Butyl acrylate and styrene (Sinopharm, 97%) was passed through a basic alumina column to remove inhibitor and stored at -20 °C. Dimethylformamide (DMF, Sinopharm, AR) and anisole (Sinopharm, AR) was dried with anhydrous magnesium sulfate and then distilled under reduced pressure prior to use. 3-Bromo-1-propyne, Dichloromethane (DCM), tetrahydrofuran (THF), anisole and triethylamine (TEA) from Sinopharm were distilled over CaH₂ just prior to use. Copper(I) bromide (CuBr, Alfa, 98%) was washed with glacial acetic acid to remove soluble oxidized species, filtrated, washed with ethanol and dried under vacuum. Sodium azide (NaN₃, Aldrich, 99%), tin(II)-2-ethylhexanoate (Sn(EH)₂, Aladdin, 95%), Ethyl α -bromoisobutyrate (Aladdin, 98%), (PMDETA, Aldrich, 99%), Tris(2-(dimethylamino)-ethyl)amine (Me₆TREN, aladdin, 98%), trifluoroacetic acid (Aladdin, 98%), diethyl ether (Sinopharm, 99.8%) and methanol (Sinopharm, 99.8%) were used as received.

Analytical Methods. NMR spectra were recorded at 300 K on a Bruker Avance III Ascend 500 (500 MHz) spectrometer with a delay time (d1) set to 8 s by using deuterated chloroform (CDCl₃) as solvent and tetramethylsilane (TMS) as the internal standard. For measurement in aqueous solution, deuterium oxide (Na₂CO₃, D₂O) was used as the solvent.

Triple-detection Size-exclusion Chromatography (TD-SEC). The absolute peak molar masses and weight-average molar masses (M_p and M_w) of comb-like polymers and other intermediate samples were measured by a triple-detection size-exclusion chromatography (TD-SEC) system. The TD-SEC system is equipped with refractive index detector (RI), the multi-angle light scattering detector (MALS), and the viscosity detector at 35 °C. The instrumentation consists of a Waters 1515 Isocratic HPLC pump with 5 mm Waters Styragel columns (guard, HR6, HR4, and HR2; the efficient exclusion limit for the HR columns are 2 × 10⁵ ~ 1 × 10⁷ g/mol, 5 × 10³ ~ 6 × 10⁵ g/mol and 5 × 10² ~ 3 × 10⁴ g/mol, respectively), a Waters 717 PLUS Autosampler, a Waters 2414 RI detector with a wavelength of 880 nm, a 18-angle light scattering detector at a wavelength of 690 nm and 220 W power, a Wyatt Visco Star viscometer detector, and a Waters Breeze data manager. The eluent was HPLC-grade THF with a flow rate of 1.0 mL/min. Prior to injection, the sample solutions were filtered

through PTFE membranes (0.22 μ m pore size). The TD-SEC system was carefully calibrated with two polystyrene standards: 1) polystyrene standard with peak molar mass (M_p) of 4.28 × 10⁴ g/mol was used to calibrate the normalization coefficients of the 18 detectors; 2) toluene and polystyrene standards with M_p of 1.03 × 10⁶ g/mol were used to calibrate the voltage calibration constant. For quantitative study, 50 μ L of polymer solution was injected into the system, and the polymer concentration was 2 ~ 8 mg/mL for these samples depending on their molar masses.

Synthesis of Azide-terminated Polystyrene Sidechain (azide-PS₃₀). Into a 100mL dry glass tube with a magnetic stirring bar, Methyl 2-bromo-2-methylpropionate initiator (0.62 g, 3.4 mmol), Me₆tren (0.23 g, 1.0 mmol), Sn(EH)₂ (0.42 g, 1.0 mmol), styrene (34.5 g, 332 mmol) and anisole (40 mL) were added successively. After mixing thoroughly, the polymerization tube was degassed by two freeze-vacuum-thaw cycles, and CuBr (50.0 mg, 0.3 mmol) was added into the frozen solution. The polymerization tube was degassed by one more freeze-vacuum-thaw cycle before sealed under vacuum. The sealed tube was immersed into an oil bath at T = 80 °C. After the polymerization was carried out for 6.5 h, the tube was immersed in liquid nitrogen rapidly. The polymer solution was then diluted with THF and passed through a short column of neutral alumina to remove metal salt. After precipitation by the addition of polymer solution into methanol/water mixture (1/1 by volume), bromo-PS₃₀ was obtained after being dried under vacuum at T = 45 °C overnight (yield ~ 8.0 g, bromo-PS₃₀, $M_w = 3 \times 10^3$ g/mol). After purification, the resulting polymer (8 g, 2.67 mmoL) was dissolved in DMF (80 mL) at round-bottom flask, and NaN₃ (0.87 g, 13.3 mmoL) was added, the resulting solution was allowed to stir at 25 °C for 24 hours. The mixture was diluted with 16 mL of CH₂Cl₂, and the insoluble inorganic salt was removed by filtration. The

filtrate was precipitated into cold methanol/water mixture (1/1, v/v) and being dried under vacuum at T = 45 °C overnight, azide-PS₃₀ was obtained (yield 7.5 g).

Preparation of Linear Poly(tert-butyl acrylate) Backbone (PtBA). A typical experimental procedure is described below. Into a 200 mL dry glass tube with a magnetic stirring bar, Methyl 2-bromo-2-methylpropionate initiator (0.06 g, 0.3 mmol), Me₆tren (0.16 g, 0.7 mmol), Sn(EH)₂ (0.28 g, 0.7 mmol), tert-butyl acrylate (44 g, 344 mmol) and acetone (75 mL) were added successively. After mixing thoroughly, the polymerization tube was degassed by two freeze-vacuum-thaw cycles, and CuBr (2.9 mg, 0.02 mmol) was added into the frozen solution. The polymerization tube was degassed by one more freeze-vacuum-thaw cycle before sealed under vacuum. The sealed tube was immersed into an oil bath at T = 60 °C. After the polymerization was carried out for 18 h, the tube was immersed in liquid nitrogen rapidly. The polymer solution was then diluted with THF and passed through a short column of neutral alumina to remove metal salt. After precipitation by the addition of polymer solution into methanol/water mixture (1/1, v/v), PtBA precursors was obtained after being dried under vacuum at T = 45 °C overnight (yield ~ 32 g, PtBA, $M_w = 1.35 \times 10^5$ g/mol). Following the similar protocol, four PtBA samples with different molar masses were synthesized.

Conversion of PtBA into Poly(acrylic acid) (PAA). A typical experimental procedure is described below. PtBA (6 g, [tBA] = 0.39 M) was dissolved in DCM (120 mL) and hydrolyzed for 24 hours using TFA (26.7 g, [TFA] = 1.95 M) to produce PAA. At least two independent reactions were required to fully hydrolyze tert-butyl acrylate. After each hydrolysis, solvent was subsequently removed by filtration. The polymer was then washed thrice with diethyl ether and separated again. Upon the completion of the third ether

washing and filtration, the sample was drying under vacuum over night to remove any remaining volatiles. Once the polymer sample was completely dried after first hydrolysis cycle, we need to grind it into small particles to ensure adequate hydrolysis next time. Following the similar protocol, four PAA samples with different molar masses were

synthesized.

Synthesis of Poly(propargyl acrylate) (PPA). A typical experimental procedure is described below. To a solution of PAA (0.50 g, [AA] = 0.46 M) in DMF (15 mL) were added TMG (1.60 g, [TMG] = 0.93 M) and propargyl bromide (1.65 g, [propargyl bromide] = 0.93 M) under the nitrogen and ice-water bath, then the mixture was stirred at room temperature without light. After 4 hours, the reaction mixture was neutralized with acetic acid (0.42 g, 7 mmol). The resulting polymer was precipitated into methanol/water mixture (1/1, v/v), and collected by filtration. The crude product was purified three times by dissolving into THF and precipitating into methanol/water mixture (1/1, v/v). Anhydrous sodium sulfate was further added to dry the THF solution. After filtration, THF was removed by rotary evaporation under vacuum, and the resultant PPA (0.45 g) was directly dissolved into DMF to prepare a stock solution. The absolute concentration was precisely calibrated by weighting method, which was double-checked by UV-vis measurement. The stock solution was bubbled with N₂ flow and stored in glove box for future use. Following the similar protocol, four PPA samples with different molar masses were synthesized and four stock solutions were prepared.

Preparation of Benzyl Azide (BA). In a 100 mL round-bottom flask, benzyl bromide (0.297 g, 2.5 mmol) was dissolved in a mixed solution of water and acetone (10 mL/40 mL). Sodium azide (0.244 g, 3.75 mmol) was added in one portion, and the solution stirred overnight. DCM (50 mL) was added, and the organic layer separated. The aqueous layer was washed with

DCM (3 \times 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and filtered. Solvent was removed under reduced pressure to give BA (yield, 335 mg) as a yellow oil. The purity of product was quantified by ¹H-NMR (not shown). The resultant BA was further dissolved into DMF to prepare a stock solution, which was further bubbled with N₂ flow and stored in glove box for future use.

Synthesis of Comb-like Polymers via Click Coupling Reactions between Azide-PS₃₀ and PPA. In experiments, the mass concentrations of CuBr, PMDETA, Sn(EH)₂ and azide-PS₃₀ were always fixed as 3.0 g/L, 7.0 g/L, 32 g/L and 200 g/L in the reaction solution, and [azide]/[alkyne] was systematically changed from 0.1 to 5. All operations were accomplished in the glove box. In one experiment, azide-PS₃₀, CuBr, PMDETA, Sn(EH)₂ and a certain amount of O₂-free DMF were first added in a small vial (5 mL) and stirred by a magnetic bar, and then a certain amount of PPA stock solution was added to start the coupling reaction. The reaction was stirred at 25 °C for 48 h. Afterwards, excess of BA ([BA]/[alkyne] = 2/1) was added to end-cap the unreacted alkyne to prevent any side reaction and enhance the stability of product during storage. After the addition of BA, the reaction was further stirred for 12 h. The reaction mixture was diluted by THF and then passed through a short column of neutral alumina to remove metal salt. Following such a protocol, comb-like samples with different molecular parameters were prepared. For PPA_{Mb}-g-PS₃₀-0 samples, twice excess of BA was directly used to react with PPA to prepared reference samples without any PS sidechains.

Table S1. Summarized molecular parameters of four PtBA precursors determined by TD-SEC.

Sample	$M_{ m w}$	$M_{ m p}$	$< M_{\rm w}/M_{\rm m}>$	Nh	
	/(g/mol)	/(g/mol)	·/// /////////////////////////////////	140	
PtBA ₈₀	1.03×10^{4}	1.15×10^{4}	1.09	80	
PtBA690	8.83×10^{4}	9.23×10 ⁴	1.02	690	
PtBA1050	1.34×10^{5}	1.47×10^{5}	1.08	1050	
PtBA2700	3.45×10^{5}	3.59×10 ⁵	1.07	2700	

Table S2. Summarized molecular parameters of four PPA_{Nb}-g-PS₃₀-0 determined by TD-SEC.

Sample	$M_{ m w}$	$M_{ m p}$	$<\!\!M_{\rm w}\!/\!M_{\rm n}\!>$	N_{b}	(dn/dc)	$R_{ m g,\sigma}/ m nm$		[η]/(mL/g)	
	/(g/mol)	/(g/mol)			/(mL/g)	average	peak	average	peak
PPA90-g- PS30-0	2.18×10^{4}	2.30×10 ⁴	1.08	90	0.157	_ a	- ^a	10.3	8.4
PPA ₆₂₀ -g- PS ₃₀ -0	1.51×10^{5}	1.56×10^{5}	1.06	620	0.157	10.7	8.7	19.9	23.5
PPA ₁₀₅₅ -g- PS ₃₀ -0	2.56×10^{5}	2.67×10^{5}	1.05	1055	0.157	12.6	11.9	33.5	35.1
PPA ₂₇₅₀ -g- PS ₃₀ -0	6.68×10^{5}	6.80×10 ⁵	1.10	2750	0.157	22.9	22.0	74.2	72.5

^a The size is too small to be accurately determined.

Table S3 Summary of molecular parameters of comb-like polymers (PPA₉₀-g-PS₃₀- σ) with different grafting density.

	$M_{ m w}$	$M_{ m p}$	< <u>M</u> /M >	dn/dc	[η] /(mL/g)		
11A90-g-1 330-0	/(g/mol)	/(g/mol)	M_W/M_n	/(mL/g)	average	peak	
PPA90-g-PS30-0.10	5.09×10 ⁴	4.81×10^{4}	1.11	0.173	15.4	13.4	
PPA90-g-PS30-0.20	7.62×10^{4}	7.59×10^{4}	1.10	0.178	14.2	13.1	
PPA90-g-PS30-0.29	1.02×10^{5}	9.76×10 ⁴	1.04	0.180	14.1	12.9	
PPA90-g-PS30-0.37	1.21×10 ⁵	1.18×10^{5}	1.06	0.181	15.3	13.1	
PPA90-g-PS30-0.44	1.46×10 ⁵	1.35×10 ⁵	1.07	0.182	15.0	12.8	
PPA90-g-PS30-0.54	1.70×10^{5}	1.59×10 ⁵	1.06	0.183	15.3	12.7	
PPA90-g-PS30-0.58	1.76×10 ⁵	1.71×10^{5}	1.05	0.183	15.2	12.5	
PPA90-g-PS30-0.69	2.08×10 ⁵	1.99×10 ⁵	1.05	0.184	14.3	12.0	
PPA90-g-PS30-0.78	2.31×10 ⁵	2.23×10 ⁵	1.05	0.184	15.1	12.1	
PPA90-g-PS30-0.81	2.33×10 ⁵	2.31×10 ⁵	1.07	0.184	15.6	12.5	
PPA90-g-PS30-0.96	2.85×10 ⁵	2.69×10 ⁵	1.06	0.184	17.0	12.1	
PPA90-g-PS30-0.97	2.91×10 ⁵	2.73×10 ⁵	1.08	0.184	14.0	11.5	

PPA ₆₂₀ -g-PS ₃₀ -σ	$M_{ m w}$	$M_{ m p}$	<m m=""></m>	dn/dc	$R_{ m g,\sigma}/ m n$	m	[η] /(mL/g)	
	/(g/mol)	/(g/mol)	M_W/M_n	/(mL/g)	average	peak	average	peak
PPA ₆₂₀ -g-PS ₃₀ -0.08	3.01×10 ⁵	3.05×10 ⁵	1.04	0.171	8.7	7.7	36.9	35.3
PPA ₆₂₀ -g-PS ₃₀ -0.18	4.77×10^{5}	4.80×10^{5}	1.03	0.177	13.5	12.1	39.9	38.4
PPA620-g-PS30-0.18	4.95×10^{5}	4.90×10 ⁵	1.05	0.177	11.2	11.9	38.4	38.1
PPA ₆₂₀ -g-PS ₃₀ -0.32	7.43×10^{5}	7.60×10^{5}	1.04	0.181	18.4	17.1	39.9	39.0
PPA620-g-PS30-0.41	8.94×10^{5}	9.25×10 ⁵	1.02	0.182	17.9	17.4	39.3	38.7
PPA ₆₂₀ -g-PS ₃₀ -0.49	9.35×10 ⁵	1.06×10^{6}	1.04	0.182	18.4	18.2	40.4	38.9
PPA ₆₂₀ -g-PS ₃₀ -0.58	1.15×10^{6}	1.22×10^{6}	1.05	0.183	21.2	20.1	39.6	38.6
PPA620-g-PS30-0.68	1.31×10^{6}	1.41×10^{6}	1.05	0.184	21.1	20.5	40.5	38.1
PPA ₆₂₀ -g-PS ₃₀ -0.68	1.35×10^{6}	1.41×10^{6}	1.04	0.184	21.3	20.8	40.0	38.7
PPA ₆₂₀ -g-PS ₃₀ -0.73	1.48×10^{6}	1.50×10^{6}	1.05	0.184	22.2	21.4	40.2	38.1
PPA ₆₂₀ -g-PS ₃₀ -0.94	1.82×10^{6}	1.89×10^{6}	1.03	0.184	24.7	24.6	38.3	37.0
PPA ₆₂₀ -g-PS ₃₀ -0.94	1.80×10^{6}	1.88×10^{6}	1.01	0.184	24.2	23.8	42.0	38.5

Table S4. Summary of molecular parameters of comb-like polymers (PPA₆₂₀-g-PS₃₀- σ) with different grafting density.

Table S5. Summary of molecular parameters of comb-like polymers (PPA₁₀₅₅-*g*-PS₃₀- σ) with different grafting density.

DDA a DS a	$M_{ m w}$	$M_{ m p}$	<m m=""></m>	dn/dc	$R_{ m g,\sigma}/ m n$	m	[η] /(mL/g)	
11A1055-g-1 530-0	/(g/mol)	/(g/mol)	<i>\M_w/M_n</i>	/(mL/g)	average	peak	average	peak
PPA ₁₀₅₅ - <i>g</i> -PS ₃₀ -0.08	5.21×10 ⁵	5.47×10 ⁵	1.06	0.171	18.6	17.6	54.0	52.2
PPA ₁₀₅₅ -g-PS ₃₀ -0.16	7.93×10 ⁵	8.25×10^{5}	1.05	0.176	19.8	19.9	56.7	56.3
PPA ₁₀₅₅ -g-PS ₃₀ -0.18	8.25×10 ⁵	852×10 ⁵	1.04	0.177	21.5	20.0	55.9	56.1
PPA ₁₀₅₅ -g-PS ₃₀ -0.30	1.21×10^{6}	1.26×10^{6}	1.04	0.180	24.3	24.5	57.1	57.5
PPA ₁₀₅₅ -g-PS ₃₀ -0.43	1.55×10^{6}	1.68×10^{6}	1.04	0.182	27.5	27.9	56.1	57.4
PPA ₁₀₅₅ - <i>g</i> -PS ₃₀ -0.51	1.84×10^{6}	1.96×10^{6}	1.05	0.183	28.6	29.1	60.9	57.7
PPA ₁₀₅₅ - <i>g</i> -PS ₃₀ -0.55	1.94×10^{6}	2.09×10^{6}	1.03	0.183	30.2	30.6	56.7	57.3
PPA ₁₀₅₅ -g-PS ₃₀ -0.62	2.16×10^{6}	2.33×10^{6}	1.03	0.183	31.4	31.7	57.4	56.6
PPA ₁₀₅₅ - <i>g</i> -PS ₃₀ -0.74	2.44×10^{6}	2.72×10^{6}	1.04	0.184	33.3	34.0	55.5	57.0
PPA ₁₀₅₅ -g-PS ₃₀ -0.80	2.47×10^{6}	2.92×10^{6}	1.04	0.184	35.0	35.4	54.5	56.5
PPA ₁₀₅₅ -g-PS ₃₀ -0.87	2.85×10^{6}	3.15×10^{6}	1.03	0.184	36.3	36.6	55.5	56.0
PPA ₁₀₅₅ -g-PS ₃₀ -0.93	3.25×10^{6}	3.32×10^{6}	1.01	0.184	34.7	35.4	57.2	56.4

PPA ₂₇₅₀ -g-PS ₃₀ -σ	$M_{ m w}$	$M_{ m p}$	<m m=""></m>	dn/dc	$R_{ m g,\sigma}/ m n$	m	[η] /(mL/g)	
	/(g/mol)	/(g/mol)	M_W/M_n	/(mL/g)	average	peak	average	peak
PPA ₂₇₅₀ -g-PS ₃₀ -0.08	1.25×10^{6}	1.31×10^{6}	1.05	0.171	32.7	30.6	122.3	97.8
PPA ₂₇₅₀ -g-PS ₃₀ -0.15	2.04×10^{6}	1.92×10^{6}	1.04	0.176	39.5	39.4	123.4	99.6
PPA ₂₇₅₀ -g-PS ₃₀ -0.30	3.36×10^{6}	3.11×10^{6}	1.06	0.180	49.7	48.7	112.0	96.6
PPA ₂₇₅₀ -g-PS ₃₀ -0.31	3.36×10^{6}	3.15×10^{6}	1.05	0.180	49.7	49.3	108.3	99.1
PPA ₂₇₅₀ -g-PS ₃₀ -0.40	3.91×10 ⁶	3.89×10^{6}	1.08	0.182	53.1	51.0	108.4	97.1
PPA ₂₇₅₀ -g-PS ₃₀ -0.41	4.14×10^{6}	3.96×10^{6}	1.08	0.182	54.1	52.8	102.4	97.6
PPA ₂₇₅₀ -g-PS ₃₀ -0.48	4.77×10^{6}	4.52×10^{6}	1.07	0.182	57.9	55.6	108.3	99.3
PPA ₂₇₅₀ -g-PS ₃₀ -0.51	5.08×10^{6}	4.72×10^{6}	1.07	0.183	58.1	56.9	109.5	101.1
PPA ₂₇₅₀ -g-PS ₃₀ -0.59	5.58×10^{6}	5.41×10^{6}	1.09	0.183	61.2	58.6	108.9	102.4
PPA ₂₇₅₀ -g-PS ₃₀ -0.63	5.99×10 ⁶	5.72×10^{6}	1.08	0.183	63.6	60.9	107.4	100.3
PPA ₂₇₅₀ -g-PS ₃₀ -0.77	7.46×10^{6}	6.82×10^{6}	1.10	0.184	69.1	67.3	101.5	97.7
PPA ₂₇₅₀ -g-PS ₃₀ -0.88	7.89×10^{6}	7.76×10^{6}	1.09	0.184	69.0	67.0	100.5	96.2

Table S6. Summary of molecular parameters of comb-like polymers (PPA₂₇₅₀-g-PS₃₀- σ) with different grafting density.



Figure S1. ¹H-NMR spectrum of azide-PS₃₀ sidechain, where the inset shows the corresponding SEC curve (M_w , M_p , M_n determined by SEC are 3.14×10^3 g/mol, 3.01×10^3 g/mol and 2.73×10^3 g/mol, respectively). The molar masses determined by ¹H-NMR spectra is 2.56×10^3 g/mol.



Figure S2. SEC curves of four PtBA precursors.



Figure S3. ¹H-NMR spectra of $PtBA_{620}$ and PPA_{620} in CDCl₃, and PAA_{620} in D₂O (Na₂CO₃, aq).



Figure S4. SEC curves of PtBA₆₂₀, PPA₆₂₀ and PPA₆₂₀-g-PS₃₀-0.



Figure S5. Plots of $[Kc/R(\theta)]$ versus $\sin^2(\theta/2)$ for PPA₁₀₅₅-g-PS₃₀- σ samples with different grafting densities (σ) by fitting the peak data in SEC curves, where σ varies from 0 to 0.93 (from top to bottom).



Figure S6. TD-SEC signals of two narrowly distributed PS standards in THF, where the peak molar masses (M_{peak}) of PS_L and PS_S are 1.03×10^6 g/mol and 4.28×10^4 g/mol based on the information provided by supplier, respectively, and the theoretical value of $R_{\text{g,peak}}$ for PS_L was calculated according to the scaling relation $R_{\text{g}}^{\text{THF}} = 2.45 \times 10^{-2} M^{0.546}$ reported in literature.¹ The inset shows the Zimm plot of peak data for PS_L.



Figure S7. Plot of increment of refractive index (Δn) versus concentration (*c*) for azide-PS₃₀, P*t*BA and PPA₁₀₅₅-*g*-PS₃₀-0 in THF at *T* = 25 °C.



Figure S8. (a) Theoretical plot of refraction index increment (dn/dc) versus grafting density (σ) according to eq S3, where $M_{0,b} = 243$ g/mol, $M_{0,g} = 104$ g/mol, $N_b = 960$, $N_g = 26$, $(dn/dc)_{backbone} = 0.157$ mL/g, $(dn/dc)_{graft} = 0.187$ mL/g were used in the plot. (b) Theoretical plot (black solid line) of average molar mass of comb-like polymers (M_{comb}) versus refraction index increment (dn/dc) for PPA₁₀₅₅-g-PS₃₀- σ samples according to eq S4, where $M_{0,b} = 243$ g/mol, $N_b = 960$, $(dn/dc)_{backbone} = 0.157$ mL/g, $(dn/dc)_{graft} = 0.187$ mL/g were used in the plot, where the dashed colorful lines represent the theoretical plots according to eq S5, and the prefactors (Γ) were determined during the analysis processes of TD-SEC data.



Figure S9. Plots of measured peak and average molar masses (M_p and M_w) versus grafting density (σ) for PPA_{Nb}-g-PS₃₀- σ samples.



Figure S10. Plot of experimentally determined grafting density (σ) versus feed ratio ([Azide]/[Alkyne]) for PPA_{Nb}-g-PS₃₀- σ samples.



Figure S11. Backbone length (N_b) dependence of the platform intrinsic viscosity ($[\eta]_{plat}$) for comb-like chains based on M_w and M_p data.



Figure S12. (a) and (b) Grafting density (σ) dependence of the chain size ($R_{g,\sigma}$) for comb-like chains with different backbone lengths (N_b) based on M_w and M_p data.



Figure S13. Grafting density (σ) dependence of normalized chain size $[R_{g,\sigma}/(N_b/620)^{\alpha}]$ for comb-like chains with different backbone lengths (N_b) based on M_w and M_p data.

Supplementary References

1. Fetters, L. J.; Hadjichristidis, N.; Lindner, J. S.; Mays, J. W. Molecular Weight Dependence of Hydrodynamic and Thermodynamic Properties for Well-Defined Linear Polymers in Solution. *J. Phys. Chem. Ref. Data.* **1994**, *23* (4), 619-640.